



Iron(III)-polyphosphates as catalysts for the liquid redox sulfur recovery process

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ARTICLE INFO

Article history:

Received 4 November 2016

Received in revised form 20 January 2017

Accepted 6 February 2017

Available online 8 February 2017

Keywords:

Iron(III)-polyphosphates

New and stable LRSR catalysts

Liquid redox sulfur recovery

Hydrogen sulfide abatement

Iron(III)-nitritotriacetate

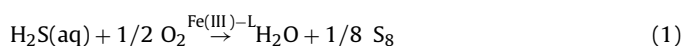
ABSTRACT

The liquid redox sulfur recovery (LRSR) process employs chelated iron(III) (Fe(III)-L; L=aminocarboxylate) as a catalyst for the air oxidation and removal of hydrogen sulfide (H₂S) from gaseous streams. One of the major disadvantages of this process is the degradation of the chelating agent via hydroxyl radical (•OH) reactions generated in the redox iron cycle and the precipitation of iron. The objectives of this investigation were to show that: a) Fe(III)-L can be replaced by iron(III)-polyphosphates (Fe(III)-PP), and b) Fe(III)-PPs are highly stable, do not degrade easily because polyphosphates react slowly with •OH, and act as true catalysts in the LRSR process. Approximately 34% of Fe(III)-L (5 mM) was destroyed catalyzing air oxidation of about 115 mM H₂S in borate buffer (pH 9) solution, and the fraction destroyed reached to about 100% when the process was carried out in unbuffered solution; while iron(III)-polyphosphate showed very little, if any, sign of degradation under similar conditions.

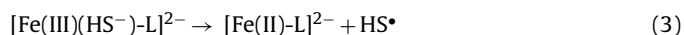
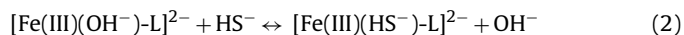
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1. Introduction

The liquid redox sulfur recovery (LRSR) process employing chelated iron(III) Fe(III)-L (L=ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA), and other aminocarboxylate) catalysts is being used to remove hydrogen sulfide, H₂S, from natural gas, refinery flue gas, etc. [1–7]. In this process, a solution containing Fe(III)-L at ambient temperature, 20–25 °C, absorbs H₂S from the gas phase and oxidizes it into elemental sulfur according to the following overall reactions:



The first step in this process is the formation of sulfhydryl radical, HS• [8], which is generated [9–12] according to the following reactions:



The pK_a of HS• radical is not known, but it is thought to be lower than 7 [8,13], and it exists mainly as sulfide radical, S•[−], in solution

at pH ≥ 7. Both of these radicals decay spontaneously – by dimerization and by addition to HS[−] – and form disulfide ion, –S₂^{2−}. The oxidation of S₂^{2−} by S•[−] radicals and/or by Fe(III)-L generates higher poly-sulfide ions and, ultimately, elemental sulfur [8,12]. In addition, the sulfide, disulfide, and higher poly-sulfides can also react with O₂ [7] and generate sulfur oxyanions.

The Fe(II)-L produced in Reaction (3) reacts with O₂, regenerating Fe(III)-L and producing hydrogen peroxide (H₂O₂); the latter reacts with Fe(II)-L and generates hydroxyl radicals (•OH) [2,3].



The •OH reacts very fast ($k = (4 - 23) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, [14]) with aminocarboxylates and initiates a cascade of reactions that can ultimately lead to the mineralization of the chelating agent, precipitation of iron and loss of catalyst [2,5], and contamination of elemental sulfur with iron oxyhydroxide. Attempts have been made to increase the useful life of Fe(III)-L by synthesizing chelating agents that are more resistant to •OH attack [4,5] and/or using •OH scavengers [2,3]. These strategies are able to increase the catalysts' useful life; however, they do not prevent their degradation.

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Sodium polyphosphates (NaPP) – for example, sodium tripolyphosphate (NaTPP), sodium tetrapolyphosphate (NaTPP), and sodium hexametaphosphate (NaHMP) – form a stable complex with Fe(III). The reduction potential of Fe(III)-TPP [15,16] is comparable to those of Fe(III)-L [4,16,17] and it is expected to be, at least, thermodynamically as effective a catalyst for the LRSR process as Fe(III)-L. The objectives of this study were to show that Fe(III)-tetrapolyphosphate – Fe(III)-TPP – and Fe(III)-hexametaphosphate – Fe(III)-HMP – can be used as catalysts for the air/O₂ oxidation of H₂S and that they are highly stable and do not suffer from the disadvantages of Fe(III)-L catalysts. The data presented in this paper shows that about 34% of Fe(III)-NTA (5 mM) was degraded catalyzing air oxidation of 115 mM of HS[−] in a borate buffer solution (pH 9), and the fraction degraded reached to about 100% in an unbuffered solution. In contrast, very little, if any, of Fe(III)-TPP/HMP were destroyed under similar conditions.

2. Material and methods

2.1. Materials

Iron(III) sulfate (97% purity), sodium hexametaphosphate (NaHMP) (96% purity), and sodium sulfide nonahydrate (Na₂S·9H₂O; 99% purity) were obtained from Sigma-Aldrich; nitrilotriacetic acid (99% purity) was obtained from Fisher Scientific; and sodium tetrapolyphosphate (NaTPP) (98% purity) was obtained from BOC Science. They were used without further purifications. All solutions were prepared in Milli-Q water.

The stock solution of Fe(III) was prepared by dissolving ferric sulfate in 0.1 M H₂SO₄ solution; stock solutions of NTA, NaTPP, and NaHMP were prepared from the corresponding acid and sodium salts, respectively. The stock solution of sulfhydryl ion (0.45 M) was prepared by dissolving Na₂S·9H₂O in Milli-Q water. Solutions of Fe(III)-TPP (1:2 Fe(III):TPP mole ratio), Fe(III)-HMP (1:1 Fe(III):HMP mole ratio), and Fe(III)-NTA (1:2 Fe(III):NTA mole ratio) were prepared by mixing the required volumes of stock solutions of Fe(III) and appropriate ligand in Milli-Q water.

2.2. Catalytic air/O₂ oxidation of HS[−] in borate buffer solution

Approximately 100–150 mL of a borate buffered solution (pH ~9) containing 5 mM Fe(III)-TPP or Fe(III)-NTA was added to an Erlenmeyer flask, spiked with 10–15 mM of HS[−], mixed well employing a magnetic stirrer, and allowed – approximately 4–5 h – the oxidation of sulfide in contact with air/O₂ to go to completion. The addition of HS[−] was repeated a number of times. The total amount of HS[−] oxidized was about 11.5 m mole. The weight of the elemental sulfur generated at the end of the test was determined by filtration method [18] using a microfiber glass filter from VWR (d = 2.4 cm, Grade 696, Cat. No. 28333-135). The filtrate was analyzed for concentration of catalyst.

2.3. Catalytic air oxidation of HS[−] in non-buffered solution

Approximately 50 mL of a solution (pH ~6.0) containing Fe(III)-TPP (1.25×10^{-2} M) or Fe(III)-NTA (3×10^{-2} M) was added to an Erlenmeyer flask, spiked with 3.2–4.8 mM of HS[−] per mM of catalyst, mixed well employing a magnetic stirrer, and allowed the oxidation of sulfide in contact with air to go to completion. The solution pH – increased with the addition, and oxidation, of HS[−] – was then adjusted to about 7.0. The addition of HS[−] was repeated several times. An aliquot (≤ 1 mL) of the supernatant was withdrawn intermittently for determination of catalyst concentration.

2.4. Catalytic oxidation of HS[−] with hydrogen peroxide

Approximately 50 mL of a solution (pH ~6.0) containing Fe(III)-TPP (1.52×10^{-2} M) or Fe(III)-HMP (3.83×10^{-2} M) was added to an Erlenmeyer flask, spiked with (equimolar to catalyst) HS[−], and adjust the solution pH – increases with the addition of HS[−] – to about 7.0–8.0. The solution was mixed well for about 2–5 min employing a magnetic stirrer, spiked with H₂O₂ (equimolar to catalyst), and allowed the oxidation of sulfide to go to completion. The addition of HS[−] and H₂O₂ were repeated several times. The concentration of catalyst was determined intermittently after the addition and oxidation of few doses of HS[−] and the amount of solid generated was measured at the end of the test following the above procedures.

2.5. Catalytic oxidation of benzoic acid with HS[−]-Fe(III)-TPP/H₂O₂

Approximately 250 mL of a borate buffer (pH 8) solution containing about 0.36 mM Fe(III)-TPP was added to a 500 mL Erlenmeyer flask, spiked with about 0.6 mM of benzoic acid (BA), mixed well and a sample was taken for the determination of initial concentration BA. To this solution was added 0.5 mM HS[−], allowed it react with Fe(III)-TPP for about 30–45 s, and then added 1.25 mM H₂O₂. A sample was taken after 30 min and both the initial and final samples were analyzed for BA.

2.6. Analytical methods

Absorption spectra were recorded employing a Cary 50 UV–vis spectrophotometer, kinetic runs were performed employing a Cary 300 UV–vis spectrophotometer, and solution pH was controlled employing sodium hydroxide (4 N) and/or hydrochloric acid (3 M).

Iron is insoluble in water under the experimental conditions unless it is complexed with NTA, NaTPP, or NaHMP; and the concentration of iron dissolved in water is equal to the concentration of chelated iron or catalyst. Therefore, the concentration of catalyst in water can be quantified by measuring the concentration of iron dissolved in water employing 1,10-phenanthroline method [18]. However, the procedure was modified slightly in that the final solution containing a known-volume of filtrate, hydroxylamine hydrochloride and 1,10-phenanthroline in ammonium acetate buffered solution was allowed to stand at least for 45 min for maximum colour development.

The HS[−] concentration was measured following the HACH Methylene Blue Method 8131 procedures. The concentrations of benzoic acid was determined by reverse phase chromatography, consisting of a Waters Associates Model 600-M system controller, a water 996 photodiode array detector and a Supelcosil LC-18 reverse phase column (25 cm long, 0.46 cm i. d.). The mobile phase was a mixture of acetonitrile (50%) and water (50%). The eluent flow rate was 1 mL/min and the detection wavelength was 270 nm.

3. Results and discussion

The addition of HS[−] to a solution – both the buffered and unbuffered – of Fe(III)-TPP generates an intensely blue-green-colored complex. Similar reaction between Fe(III)-L and HS[−] was also reported in the literature [19]. The complex, [Fe(III)(HS)-TPP]^{2−}, absorbs strongly in the visible region and exhibits absorption peaks at around 414 nm, 513 nm, and 611 nm. The absorption spectra of HS[−], Fe(II)-TPP, Fe(III)-TPP, Fe(II)-TPP plus HS[−], and Fe(III)-TPP plus HS[−] are shown in Fig. 1. The blue-green color appears relatively fast and decays slowly and exponentially with a first-order decay rate constant of about $(4.1 \pm 1.8) \times 10^{-4} \text{ s}^{-1}$.

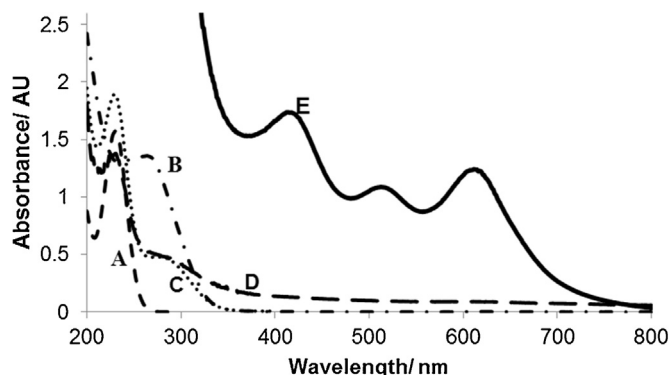


Fig. 1. Absorption spectra of (A) 0.2 mM HS[−], (B) 0.25 mM Fe(III)-TPP, (C) 0.56 mM Fe(II), (D) 0.4 mM-TPP + 0.8 mM HS[−], and (E) 1 mM Fe(III)-TPP + 2 mM HS[−] in borate buffered (pH 9.0) solution.

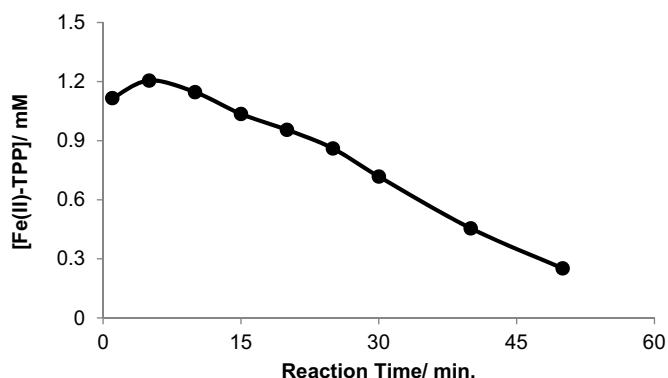


Fig. 2. Plot showing the formation and decay of Fe(II)-TPP during the air/O₂ oxidation of 2 mM HS[−] catalyzed by 2 mM Fe(III)-TPP.

in borate buffered solution at pH 9. The decay rate of the blue-green colour was found to increase by about 25% when the solution pH was reduced from about 9.0–8.0. Similar observations were also reported for Fe(III)-EDTA [1]. The disappearance of blue-green colour is accompanied by the appearance of yellowish colloidal sulfur. The complex generated with Fe(III)-HMP exhibits absorption peaks and/or shoulders at 609 nm, 507 nm, and 413 nm.

The molar absorption coefficient of [Fe(III)(HS)-TPP]^{2−} complex at 611 nm was determined following the procedures provided by Agren [21] and was found to be about 6320 M^{−1} cm^{−1} (see Text and Fig. S1, Supplementary Information (SI)). The rate constant of the reaction between HS[−] and [Fe(III)-TPP]^{2−} was quantified by measuring the rate of growth of absorbance at 611 nm (see Text and Fig. S2, SI) and was found to be $k = 0.8 \pm 0.2 \text{ M}^{-1} \text{ s}^{-1}$ (average of three measurements).

As discussed earlier, the [Fe(III)(HS)-TPP]^{2−} complex decomposes to Fe(II)-TPP and HS• (H⁺/S^{•−}). The data presented in Fig. 2 shows that Fe(II)-TPP forms rapidly and decays slowly. The HS•/S^{•−} decay spontaneously to S₂^{2−}, which in turn reacts rapidly with HS[−] and/or Fe(III)-TPP and oxidizes to higher polysulfide ions and, ultimately, elemental sulfur [8,12,13]. The amount of solid generated from the oxidation of about 11.5 m moles of HS[−] (368 mg as S^{2−}) was about 140–160 mg (~42 ± 3% recovery) with Fe(III)-NTA (about 0.05 mM or 31 mg) and 20–80 mg (~5%–22% recovery) with Fe(III)-TPP (0.05 mM or 40.6 mg) catalysts; the lower yield was obtained when the solution was gently bubbled with oxygen or air. It is assumed that the remaining sulfhydryl ion was oxidized to sulfur oxyanions because O₂ reacts very fast with S^{•−} ($k = 7.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, [12]) and that the reaction between O₂ and

S^{•−} can compete effectively with the spontaneous decay of S^{•−} to disulfide and higher polysulfide and generate sulfur oxyanions.



The rate of oxidation of HS[−] by air/O₂ (see Text and Fig. S3, SI) catalyzed by Fe(III)-NTA ($k_{\text{app}} = (6.2 \pm 0.1) \times 10^{-2} \text{ s}^{-1}$) is about twenty times faster than that catalyzed by Fe(III)-TPP ($k_{\text{app}} = (3.3 \pm 0.6) \times 10^{-3} \text{ s}^{-1}$). This is attributed to the slower rate of oxidation of Fe(II)-TPP with O₂ and the regeneration of Fe(III)-TPP [16]. Therefore, it is reasonable to assume that the rate of generation of HS•/S^{•−} with Fe(III)-NTA catalyst is also that much faster than that with Fe(III)-TPP; and at lower concentrations, the reaction between S^{•−} with O₂ – Reaction (6) – can compete effectively with the spontaneous decay of S^{•−} to disulfide and higher poly-sulfides, resulting in a lower yield of elemental sulfur.

The dried solid from the air/O₂ oxidation of HS[−] catalyzed by Fe(III)-NTA but not by Fe(III)-TPP (see Fig. S4, SI) appears to contain iron(III) oxy-hydroxide – as judged by its colour – and this could also partially account for the higher yield of solid produced with this catalyst as well. The presence of iron(III) oxy-hydroxide in the solid is attributed – as discussed above – to the generation of •OH, which reacts very fast with both the HS[−] ($k = 9.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ [14]) and Fe(III)-NTA ($k_{\text{OH,NTA}} = 2.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ [14]) and degrades/destroys Fe(III)-NTA [2].



Assuming that: a) the rate of reaction of •OH with Fe(III)-NTA is the same as that with NTA, and b) the sum of concentrations of sulfide and poly-sulfides reacting with •OH is equal to 50% of initial concentration of HS[−], then the fraction of •OH reacting with Fe(III)-NTA is estimated to be about 20% on average. In the absence of NTA, Fe(III) – insoluble in water under the experimental conditions – hydrolyzes and polymerizes rapidly and precipitates out. Analyses of the filtrates for the concentration of catalyst have shown that approximately 34% of Fe(III)-NTA was destroyed during the above tests while very little, if any, of Fe(III)-TPP was lost. The rate constant of the reaction between •OH and TPP is not known; however, the published rate constants of reaction of •OH with phosphate ($k < 1.0 \times 10^7 \text{ mol}^{-1} \text{ s}^{-1}$) and pyrophosphate (P₂O₇^{4−}, $k = 9.0 \times 10^5 \text{ mol}^{-1} \text{ s}^{-1}$) ions [13] are very low. Therefore, it is conceivable to assume that •OH does not react reasonably fast with TPP either, resulting in negligible, if any, loss of Fe(III)-TPP.

The implementation of the LRSR process in the buffered solution may or may not be possible in industry. Therefore, catalytic air/O₂ oxidation of HS[−] was also performed in unbuffered solution at room temperature. Fig. 3 shows the rate of degradation of Fe(III)-NTA and Fe(III)-TPP concentrations against the number of moles of HS[−] oxidized. The data shows that Fe(III)-NTA was destroyed during the air/O₂ oxidation of HS[−] and its concentration was reduced from about 0.03 M (~84 mg as Fe(III) in 50 mL) to $\leq 2 \times 10^{-4} \text{ M}$ (or ~0.56 mg as Fe(III) in 50 mL) after the oxidation of about 1.8×10^{-2} moles (594 mg) of HS[−] ([HS[−]]/[Catalyst] molar ratio of about 12). This is in qualitative agreement with the data reported by Chen et al. [2]. In contrast, Fe(III)-TPP appears to be very stable and, within experimental errors, its concentration ($6.5 \times 10^{-4} \text{ mol}$ or ~36.5 mg as Fe(III) in 50 mL) did not change after oxidizing about 7.2×10^{-2} moles (~2.38 g) of HS[−] ([HS[−]]/[Catalyst] molar ratio of about 110), which is four-fold higher than that oxidized in the presence of Fe(III)-NTA.

The Fe(III)-TPP/HMP catalyzed oxidation of HS[−] was also carried out in presence of H₂O₂. In these tests, the catalysts were allowed to react with HS[−] for about 2–5 min and build-up Fe(II)-TPP/HMP before adding H₂O₂. It is estimated that – using the apparent reac-

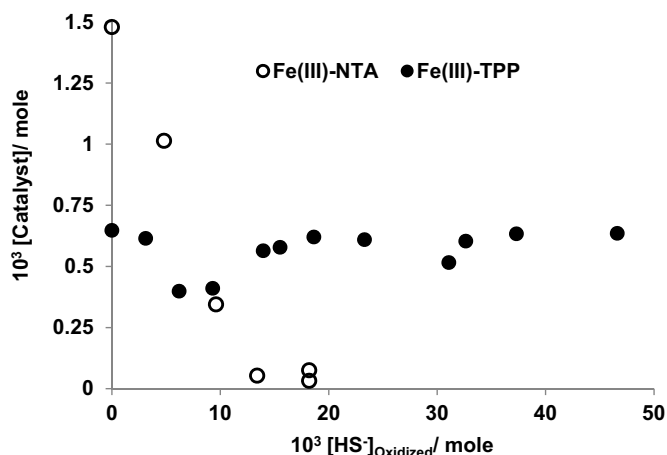


Fig. 3. Plots showing the evolution of concentrations of Fe(III)-NTA and Fe(III)-TPP catalysts during the air oxidation of HS^- as a function of HS^- concentration oxidized.

tion rate constant provided earlier – the fraction of HS^- that was oxidized to di- and poly-sulfides was about $(52 \pm 21)\%$. The fraction di- and poly-sulfides converted to elemental sulfur would have been small because of the very slow rate of redox cycling of iron. The solution blue-green colour disappeared quickly, generating elemental sulfur and sulfur oxyanions after the addition of H_2O_2 . Plots showing concentrations of Fe(III)-TPP and Fe(III)-HMP against the amount of HS^- oxidized are shown in Fig. 4. The data clearly shows that very little catalysts, if any, was oxidized in these tests. In contrast to the above observations, approximately 80% of Fe(III)-NTA (1×10^{-2} M or ~ 220 mg in 50 mL) was degraded catalyzing H_2O_2 oxidation of 0.115 mol (or ~ 3.80 g) of HS^- in borate buffered solution at pH 9 and this – as described before – is because NTA reacts very fast with $\bullet\text{OH}$ and can compete with HS^- for hydroxyl radicals.

The chelated iron(II) – Fe(II)-L – reacts very fast ($k = 3 \times 10^3 - 2 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ [21]) with H_2O_2 as does hydrolyzed species of Fe(II) ($k = (1.7 \pm 0.1) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ [22]). It is conceivable to assume that Fe(II)-TPP/HMP also reacts very fast with H_2O_2 . Perhaps it is for this reason – i.e., the fast reaction between Fe(II)-TPP and H_2O_2 , Reaction (11) – that the solution colour disappears very fast following the addition of H_2O_2 in the above test since

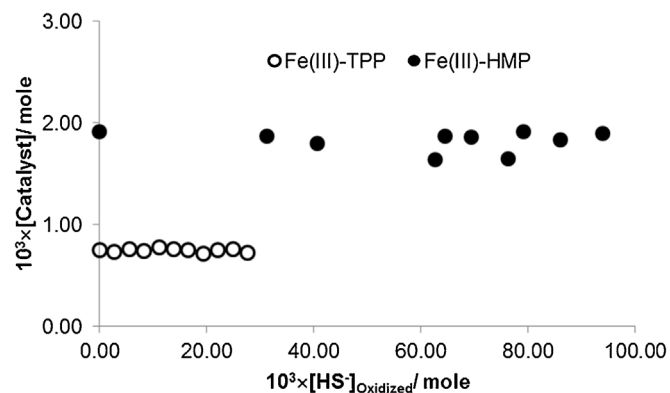
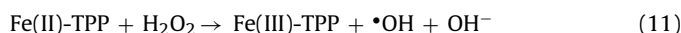


Fig. 4. Plots showing the concentration of the catalysts for the H_2O_2 -induced oxidation of HS^- vs the concentration of HS^- oxidized.

Fe(III)-TPP – as the data presented in Fig. 5 demonstrates – reacts fast with hydrogen peroxide.



The data presented in Fig. 5 shows that H_2O_2 degrades instantaneously following the addition HS^- . The $\bullet\text{OH}$ radicals generated in Reaction (11) react with HS^- (Reaction (9)), speeding the rate of generation of di- and poly-sulfides and their conversion to elemental sulfur. The data presented in Fig. 5 also shows that the catalytic oxidation of two mM of HS^- was accompanied by the disappearance of about 3.4 mM of H_2O_2 ; this is less than the theoretical value of 4 [8], indicating that approximately 85% of HS^- was oxidized to elemental sulfur and the rest was converted to sulfur oxyanions.

The H_2O_2 oxidation of HS^- catalyzed by Fe(III)-TPP – in borate buffered (pH ~ 9) solution – was also carried out in the presence benzoic acid (BA). Analyses of the samples collected before and after the addition of HS^- have shown that approximately, $19.5 \pm 2.6\%$ (average for four experiments) of BA was removed and *p*-hydroxybenzoic acid was one of the oxidation by-products of BA. This observation further confirmed that $\bullet\text{OH}$ was produced in this system [23,24].

The sulfhydryl radical also reacts with H_2O_2 and oxidizes to elemental sulfur [25]. In order to examine the role of non-catalytic oxidation of sulfhydryl ion in the above tests, the kinetics of oxidation of HS^- by H_2O_2 in borate buffered solution (pH ~ 9) was carried out under the pseudo-first order conditions using excess

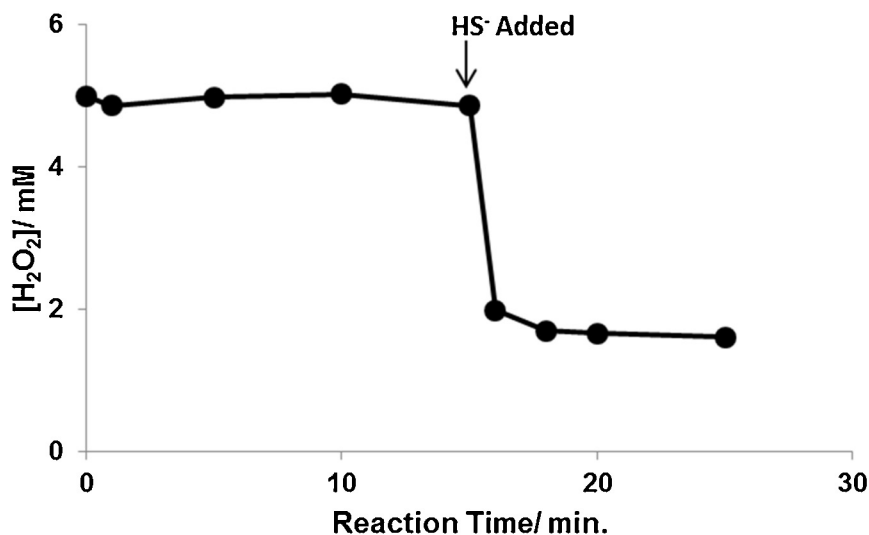


Fig. 5. Plot showing the rate of decomposition of H_2O_2 (5 mM) catalyzed by Fe(III)-TPP (1 mM) in the absence and presence HS^- (2 mM) in borate buffered (pH ~ 8) solution.

H₂O₂. The HS[−] concentration was found to decay exponentially and the pseudo-first order rate constant varied linearly with varying concentration of H₂O₂ (see Text and Fig. S5, SI), yielding a second-order rate constant of $k = 0.40 \pm 0.09 \text{ M}^{-1} \text{ s}^{-1}$ for the oxidation of HS[−] by H₂O₂. This is in agreement with the mechanism of oxidation of H₂S by H₂O₂ in the buffered neutral solution [25]. The rate of reaction of H₂O₂ with HS[−] is orders of magnitudes slower than that with Fe(II)-TPP/HMP and it is expected to be even slower under the experimental conditions (pH ~7.0–8.0) [25]. The fraction of HS[−] oxidized by H₂O₂, under our experimental conditions, is estimated to be less than 5%.

Taken together, the above observations support the previous contention that polyphosphates react very slowly with •OH and explain the high stability and robustness of Fe(III)-TPP and Fe(III)-HMP complexes as catalysts for the LRSR process. The sulfur recovery from H₂O₂ oxidation of HS[−] catalyzed by Fe(III)-NTA, Fe(III)-TPP, and Fe(III)-HMP were about 78%, 61%, and 58%, respectively. The higher recovery rate with the Fe(III)-NTA catalyst is attributed, at least in part, to the presence of iron oxy-hydroxide in the solid.

A catalyst, by definition, is a compound that does not undergo any permanent chemical changes while increasing the rate of a reaction. The data presented in Figs. 3 and 4 demonstrates that iron(III)-polyphosphates (Fe(III)-PP) appear to behave like true catalysts for the air/O₂ and hydrogen peroxide-induced oxidation of sulfide, whereas iron(III)-L (where L is aminocarboxylate) undergoes permanent chemical changes and degrades during the sulfide ion oxidation process.

4. Conclusions

The LRSR process employing Fe(III)-L is a convenient and economical process for capturing H₂S from gaseous streams and recovering elemental sulfur. One of the major disadvantages of this process is that the Fe(III)-L catalysts are unstable. The stability of iron(III)-L can be increased significantly by adding •OH scavengers to the H₂S absorbing solution and/or employing ligands that do not react very fast with •OH, but it cannot be eliminated altogether. Another disadvantage of the LRSR process is that the recovered sulfur is contaminated with iron and cannot be used without further purification. The data presented in this paper shows that the air/O₂ oxidation of HS[−] can be catalyzed by Fe(III)-TPP and Fe(III)-HMP. The data also shows that these catalysts appear to be highly stable and last for a very long time. This is attributed to –by analogy to phosphate and pyrophosphate – the slow rate of reaction of TPP and HMP with •OH. In other words, Fe(III)-TPP and Fe(III)-HMP appear to act as true catalysts for the air oxidation of hydrogen sulfide. However, the rate of oxidation of HS[−] with air/O₂ catalyzed by Fe(III)-TPP is about twenty times slower than that catalyzed by Fe(III)-L. Consequently, the oxidation of a given quantity of HS[−] by Fe(III)-TPP will take that much longer time than oxidation by Fe(III)-NTA. The data also shows that the sulfur recovery with Fe(III)-TPP is lower than that with Fe(III)-L.

Acknowledgment

The authors would like to thank Dr. Mihaela Stefan for her critical review of the manuscript.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2017.02.022>.

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Further reading

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